REMARKS

New claims 22 and 23 are added which depend from claims 12 and 13, respectively, and which recite that the compound represented by formula (1) or (3) is a merocyanine compound. Support for the amendment is found, for example, based on the general formula (1) or (3) and the specific exemplary compounds disclosed in the specification as originally filed. Applicants further submit the attached reference, The Theory of the Photographic Process, 4th Ed., which shows that merocyanine dyes are different from cyanine dyes.

In response to the Advisory Action dated June 11, 2008, Applicants refer the Examiner to the Response filed June 2, 2008 and the "Remarks", which are incorporated herein by reference. Applicants further submit that the Examiner is incorrect in stating that the formula recited in the present claims embraces cyanine dyes. As shown in the attached reference, cyanine dyes are completely different from merocyanine dyes. Specifically, cyanine dyes are cationic dyes; oxonol dyes are anionic dyes; and merocyanine dyes are nonionic dyes (neutral dyes).

Applicants submit that formula (1) and (3) of the present application represent merocyanine dyes and do not include cyanine dyes.

In view of the above, and in view of the Response filed June 2, 2008, which is incorporated herein by reference, Applicants respectfully submit that the present invention is not rendered obvious by any of the cited references, whether taken alone or in combination.

Accordingly, Applicants respectfully request withdrawal of the rejections.

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the

Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

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CHAPTER
8
SENSITIZING AND DESENSITIZING DYES

D. M. STURMER AND D. W. HESELTINE

DYES ARE used in photography for a number of distinct purposes, the most important of which are (1) as spectral sensitizers (sensitizing dyes), (2) as color images in color photography, (3) in antihalation and filter layers and in color filters, and (4) as desensitizers. Dyes of categories (1) and (4) are the subject of this chapter.

A. Historical Perspective

Comprehensive reviews of sensitizing dye literature were prepared by Brooker,[1–9] Hamer,[10] Ficken,[11] Kiprianov,[12–18] and Sturmer.[19] Published proceedings of various symposia on dyes provide additional reviews of color/constitution, physical/chemical properties, and spectral sensitization.[20–28] The encyclopedic review by Hamer is outstanding and remains the best source for the preparative heterocyclic chemistry of cyanine and related dyes. Several reviews cover the history of sensitizing dyes,[1b,4,10,19] and only some of the more important events will be noted here.

Early work (1850–1910) includes the discovery of the first cyanine dye by Williams,[29] the discovery of spectral sensitization of silver halides by Vogel,[30] and the synthesis of pinacyanol, the first sensitizer for red light, by Homolka.[31] During the period 1915–1925, structural identities for several useful spectral sensitizers were established (Figure 8.1),* largely through the work of Mills and Hamer.[10,32–34] The cyanine dyes in use at that time were recognized as composed of two heterocyclic nuclei joined by a monomethine link (simple cyanines) or a trimethine link (carbocyanines).

Major synthetic advances were made during the period 1920–1960. (1) Koenig used orthoesters and vinylogs of these compounds $[\mathrm{EtO}\!\left(\mathrm{CH{=}CH}\right)_n\mathrm{CH(OEt)_2}$, $n = 0, 1]$ to prepare symmetrical dyes.[35] Variations of these reagents led to powerful sensitizers[36] [from $\mathrm{RC(OEt)_3}$] and to extended-chain dyes with seven methine carbons.[37] (2) Piggott and Rodd at ICI, Ltd., developed reagents for unsymmetrical dyes,[38] which are known as "ICI intermediates," and the analogous reagents from ketomethylene compounds were first made by Dains and coworkers.[39]

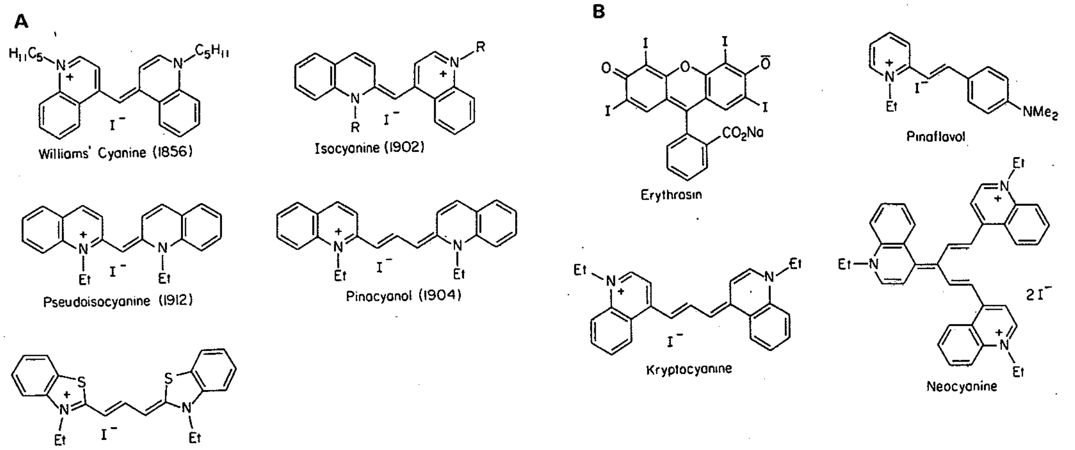

FIG. 8.1. *Structures of early spectral sensitizers.* (**A**) *Structural assignments from the period 1917–1924.* (**B**) *Commercial sensitizers in 1926 as described by Brooker* (private communication).[34]

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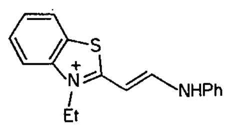
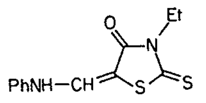
* In general, counterions for dyes are not specified in this chapter.



ICI intermediate



Dains intermediate

(3) A large class of valuable sensitizers known as **merocyanines** was developed in the early 1930s.[40,41] The dyes also served as intermediates for more complex dyes, usually incorporating two or more typical dye chromophores. (4) Extended-chain quaternary salts[42] provided important synthetic access to infrared sensitizers. The color-structure relations for symmetrical dyes were essentially dictated by the early structural work on cyanines,[10] but unsymmetrical dyes were instrumental in understanding color and constitution. Much of the early experimental work on cyanine and merocyanine dyes was published by Brooker[43–55] (Section B), although Kiprianov independently used certain similar concepts.[56–59]

During the period 1950–1966 the generalized syntheses of heterocyclic polymethine dyes were applied to other conjugated systems,[60] employing some rather novel reagents. In addition to the heterocycles in which the chromophoric nitrogens (typical of the original cyanines) are replaced by another heteroatom,[61] hydrocarbon analogs of cyanines (positive charge) and oxonols (negative charge) were prepared,[60,62] along with ferrocene-,[63] boron-,[64] and phosphorus-containing[65,66] dyes. Conjugated betaines[67] ("merocyanines") were prepared by oxidative syntheses, analogous to the many preparations of simple cyanines nearly a century earlier (1850–1920).

1. SPECTRAL SENSITIZATIONS: STATE OF THE ART

Spectral sensitizers extend the responses of photoconductors to longer wavelength and accomplish spectral separation in either the visible or infrared. Beyond the early efforts to provide spectral sensitizers for the visible spectrum (400–700 nm) and the initial color films,[68] dye synthesis since 1930 has pursued two important goals: extended wavelength sensitizations and improved color sensitizations. First, spectral sensitization was extended to wavelengths well beyond 1000 nm. This was achieved not only in experimental films but also in high quality commercial films (Figure 8.2).[69] Second, spectral sensitizers and filter dyes have been designed to meet the requirements of new color films (Chapters 11; 18; 19, Section II). The desired color separations often require dyes that sensitize over rather narrow spectral ranges with sharp decreases in spectral sensitivities at long wavelength (for example in the yellow- and magenta-forming layers of KODAK AEROCHROME Infrared Film, Type 2443, see Figure 18.2).[70] Although the achievements in these sensitizations are not solely synthetic, optimizing the spectral and physical characteristics of efficient spectral sensitizers has necessitated considerable synthetic effort.

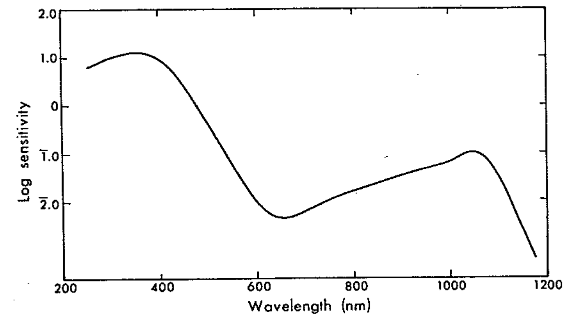


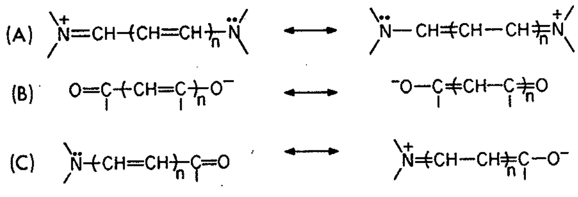
FIG. 8.2. *Spectral sensitivity for the KODAK Spectroscopic Plate, Type I–Z, hypersensitized* (reference 69). *Spectral sensitization extends beyond* 1100 nm.

B. Generic Concepts: Cyanine and Related Dyes

Most of the relationships between the color and structure of dye molecules were established before the widespread use of computers.[1,2,10,71] Brooker[72] and coworkers provided extensive documentation of the major trends with two series of publications: (1) Color and Constitution[43–55] I–XII (1940–1951), XIII (1965); and (2) Steric Hindrance[6,8] (1947–1953). Kiprianov and coworkers published parallel work independently.[12–18] Resonance theories were developed to accommodate all the major trends in a highly successful manner. For an experienced dye chemist, these still represent the most useful approach to the design of dyes with a specified color, band shape, or solvent sensitivity. More recently, the cataloguing of specific oxidation and reduction potentials has led to additional structure/property relationships and the computer-assisted design of new molecules.

1. CHROMOPHORIC SYSTEMS

Sensitizing dyes are characterized by high extinction transitions in the visible or infrared regions of the spectrum. The primary types of chromophores for these molecules are the amidinium ion system (A), the carboxyl ion system (B), and the dipolar amidic system (C).



$$\text{(A)}\quad \overset{+}{\text{N}}{=}\text{CH}{-}(\text{CH}{=}\text{CH})_n{-}\ddot{\text{N}} \longleftrightarrow \ddot{\text{N}}{-}\text{CH}{=}(\text{CH}{-}\text{CH}{=})_n\overset{+}{\text{N}}$$

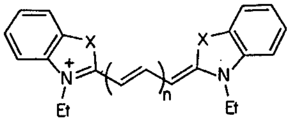
$$\text{(B)}\quad \text{O}{=}\text{C}{-}(\text{CH}{=}\text{C})_n{-}\text{O}^- \longleftrightarrow {}^-\text{O}{-}\text{C}{=}(\text{CH}{-}\text{C}{=})_n\text{O}$$

$$\text{(C)}\quad \ddot{\text{N}}{-}(\text{CH}{=}\text{CH})_n{-}\text{C}{=}\text{O} \longleftrightarrow \overset{+}{\text{N}}{=}(\text{CH}{-}\text{CH}{=})_n\text{C}{-}\text{O}^-$$

For each system two extreme resonance structures are shown, where any of the formal charges are located at the ends of the chromophore. Intermediate resonance structures, with the charges nearer the center of the chromophore, are generally considered less important, particularly in the resonance picture of symmetrical ground-state dyes. However, contributions of these intermediate forms to the first excited state may be significantly larger, suggesting that after excitation more of the formal charge is located on the methine carbons than on the terminal atoms. For the symmetrical dyes this leads to more positive (or negative) charge near the center of system A (or B). For the dipolar dyes from system C, the charge separation is less for the excited states. These resonance concepts agree qualitatively with the results from quantum mechanical calculations.

The important characteristics that influence the absorption wavelengths for these dyes are the length of the conjugated chain and the nature of the terminal group. Many of the early cyanine dyes comprised a chain with an odd number of methine carbon atoms (C—H) and two heterocyclic rings like quinoline or benzothiazole. Historically, the terms **simple cyanine, carbocyanine, dicarbocyanine**, and so on, were used to designate both the specific dyes derived from quinoline and also generic dye structures (1) from other heterocycles with one, three, five, and so on, methine carbon atoms. For the dyes from quinoline, the ring position attached to the methine chain and the N-substituent are usually specified (for example, 1,1′-diethyl-2,2′-cyanine is dye (1) with X = CH=CH and n = 0).

(I)



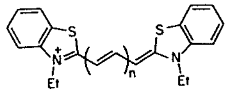
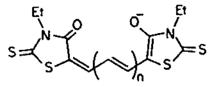
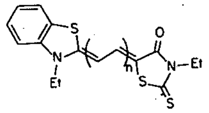
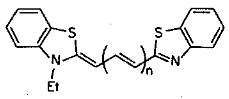
n = 0, a simple cyanine
n = 1, a carbocyanine
n = 2, dicarbocyanine
n = 3, a tricarbocyanine

Dyes derived from the primary chromophores B and C were subsequently designated **oxonols** and **merocyanines**, although the term **neutrocyanine** has also been used for C. For certain cyanine dyes and for merocyanines "simple" designation refers to a dye with zero methines, that is, the shortest possible linkage between the terminal groups that retains the chromophore.

Dyes that differ only by the number of vinyl groups (CH=CH) in the conjugated chain are termed a **vinylogous series**. Absorption maxima for several vinylogous series of dyes like (2)–(5) in Table 8.1 shift to longer wavelengths as the methine chain length increases. The shift approximates 100 nm per vinyl group in most symmetric chromophores like (2) (amidinium ion system A) and (3) (carboxyl ion system B), and these are termed **nonconverging** series. Less symmetric chromophores including those of the dipolar amidic systems (4, 5, C) and the polyenes (6) show markedly reduced shifts as each vinyl unit is added (**converging** series). In the dyes the degree of asymmetry and the absorption shifts are both related to the structures of the heterocyclic terminal groups.

TABLE 8.1

Absorptions of Vinylogous Dyes[a]

Dye		λ_{max}, nm($\epsilon \times 10^{-4}$, $\mathrm{lm^{-1}\,cm^{-1}}$)				
		n = 0	1	2	3	Ref.
	(2)	423 (8.5)	557 (15)	650 (23)	758 (25)	b
	(3)	542 (8.2)	613 (11)	714 (14)	---	c,d
	(4)	432 (6.0)	528 (9.3)	605 (8.5)	635 (6.9)	c
	(5)	396 (5.9)	458 (5.7)	490 (6.4)	510 (--)	b
$\mathrm{Ph}\text{-}(\mathrm{CH{=}CH})_n\text{-}\mathrm{Ph}$	(6)	---	328 (9)	357 (12)	383 (27)	e

[a] Spectra were obtained in methanol or ethanol for dye series (2), (3), (5), pyridine for (4), and ether-alcohol at −196° C for (6).
[b] Reference 43.
[c] Reference 52.
[d] M. V. Deichmeister, I. I. Levkoev, and E. B. Lifshits, *Zh. Obshch, Khim.*, **23**, 1529 (1953).
[e] K. W. Hausser, R. Kuhn, and G. Seitz, *Z. Physik. Chem. B*, **29**, 391 (1935).

Absorption spectra for typical symmetrical cyanine dyes exhibit a variety of band shapes (Figure 8.3). The first members of the vinylogous series (2) have a single absorption band in the visible spectrum with prominent vibrational shoulders on the short wavelength side of the band and increased extinction coefficients through n = 3. Compared to the thiatricarbocyanine (2, n = 3), infrared dyes with longer polymethine chains [(2) n = 4–5, the rigidized analogs (7) n = 1–3, and the infrared dye (8)] showed decreased extinctions for the long wavelength bands and increased absorption at shorter wavelengths. Rigidizing groups on the polymethine chain and pyridine as a nonpolar solvent both provided some increase in the absorption at long wavelengths (Figure 8.3, curves a–d). Brooker attributed these increases to a higher proportion of all-trans conformations.[3,4]

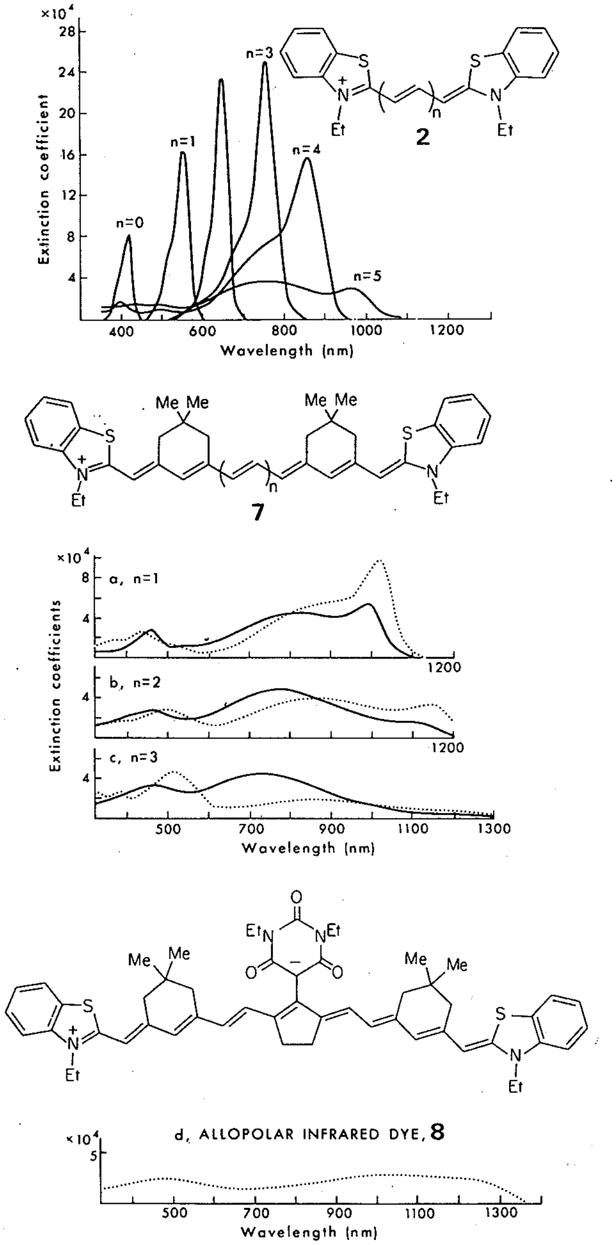
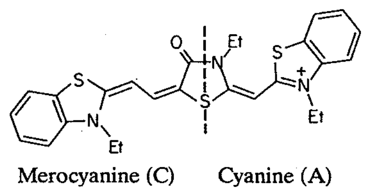


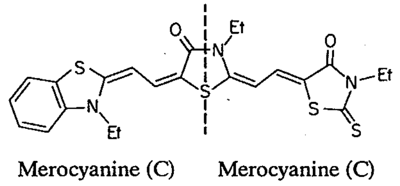
FIG. 8.3. *Absorption spectra for vinylogous series of symmetrical cyanine dyes. For methanol solutions of the thiacyanine dyes* (2), *both* $\lambda_{\max}$ *and extinction coefficient increase as the methine chain is lengthened from* $n = 0$ *to* $n = 3$; *but the vibrational shoulder on the short-wavelength side is least prominent for* $n = 3$. *Longer chain thiacyanines* ($n = 4$, 5) *show lower extinction coefficients for the longer wavelength band, and additional absorption bands in the* 600–800-nm *region. Rigidized long chain dyes* (7, $n = 1$–3) *and the allopolar infrared dye* (*structure* 8 *in Scheme* 8.1) *show increased absorption at long wavelength* (*curves a–c and d*). *Anhydrous pyridine* (· · ·) *maximizes the long-wavelength peaks relative to the spectra in methanol* (——).

Two or more of the chromophoric systems A, B, or C are incorporated in a remarkably large group of dyes. Typical combinations are shown in the structures (9)–(13).

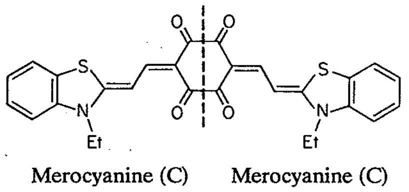
(9)



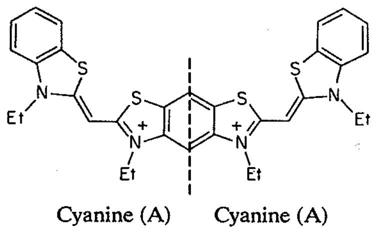
(10)



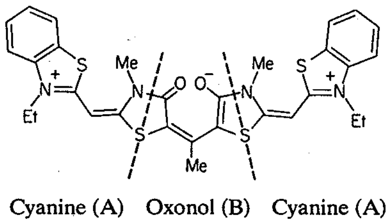
(11)



(12)



(13)



In all of these dyes the separate chromophores are conjugated through common rings. In the first two, the common ring serves as an electron acceptor for the merocyanine portion on the left side and an electron donor for the cyanine or merocyanine part on the right. In the second two the common rings serve as either electron acceptors [structure (11), merocyanine] or as electron donors [structure (12), cyanine]. The last structure, (13), incorporates an oxonol chromophore, which has common rings with two cyanine chromophores. Most dyes like these five are prepared using standard synthetic reactions[10] and multiple reactive sites on the common rings.

2. TERMINAL GROUPS

Virtually any atom or group of atoms can function as terminal groups for dyes if the nitrogens and oxygens in the primary chromophores A, B, and C